

The University of Chicago

STUDIES IN
THE DIMETHYLBUTADIENE SERIES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1937

By
KIMUEL ALONZO HUGGINS

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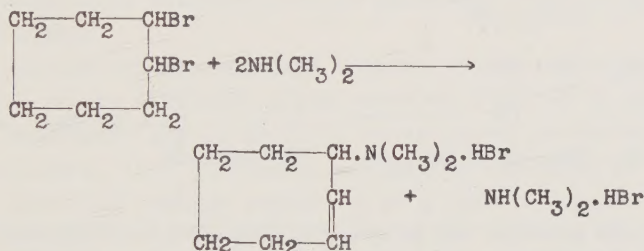
ACKNOWLEDGMENT

The writer wishes to express his deep indebtedness to Dr. Irving E. Muskat for suggesting this problem and for many helpful suggestions and encouragement given.

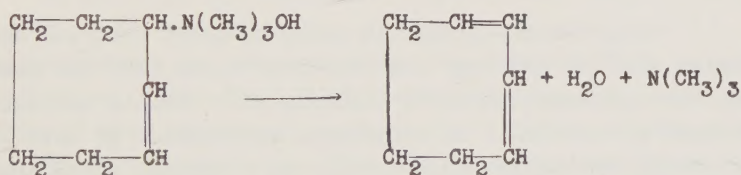


I. INTRODUCTION

The preparation of cyclobutadiene has been attempted a number of times. Willstätter and his co-workers¹ tried to apply the well-known method of exhaustive methylation and decomposition of the quaternary base to the preparation of cyclobutadiene, a method which they had successfully applied to the preparation of cycloheptadiene, cycloheptatriene² and cyclo-octene.³ The following equations illustrate the formation of cycloheptadiene and cycloheptatriene.



The Δ^2 -dimethylamine cycloheptene is converted into the quaternary ammonium iodide which in turn is converted into the hydroxide. On distillation, the hydroxide breaks up into trimethylamine, cycloheptadiene, and water.

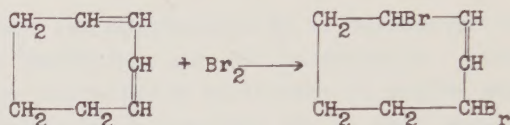


¹Willstätter, Ber., **38**, 1992 (1905); Ber., **40**, 3979-99 (1907).

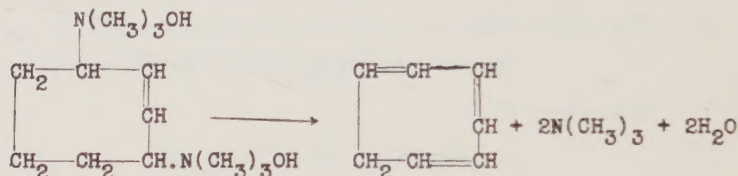
²Ibid., Ann. d. Chem., **317**, 204 (1901).

³Willstätter and Veraguth, Ber., **38**, 1984 (1905).

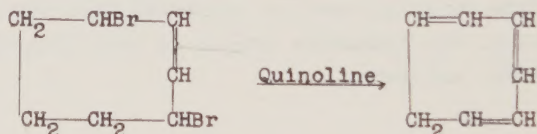
Cycloheptadiene, a compound containing a conjugated system of double bonds, reacts with bromine to form a 1,4-dibromide, from which cycloheptatriene may be obtained in two ways.



It may be combined with dimethylamine to form the corresponding diamine which, upon exhaustive methylation, gives cycloheptatriene and trimethylamine.

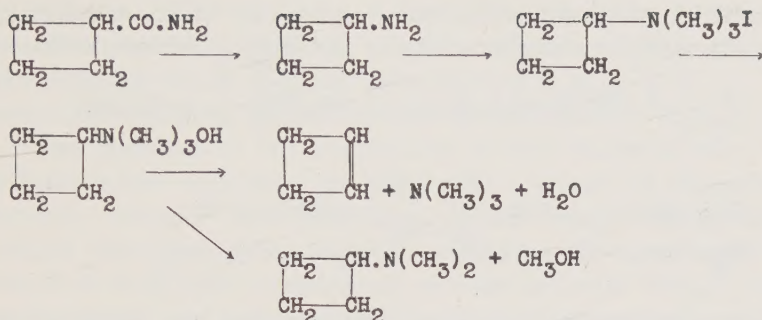


Or hydrogen bromide may be removed from the 1,4-dibromide by boiling with quinoline.



Cyclobutane-carboxylic acid, obtained from the dicarboxylic acid¹ by heating, was converted first into the amide, and then into cyclobutylamine by treating with bromine and alkali (Hofmann's reaction). By exhaustive methylation of this compound cyclobutyltrimethylammonium iodide was obtained, which upon treatment with silver oxide in aqueous solution gave the corresponding hydroxide. When cyclobutyltrimethylammonium hydroxide was distilled a mixture of water, cyclobutene, trimethylamine and cyclobutyldimethylamine was formed.

¹Perkins, J. Chem. Soc., 65, 950 (1894).



Willstatter and Bruce¹ also attempted to obtain cyclobutene by distillation of aminocyclobutane phosphate² but obtained instead butadiene.

Cyclobutene reacts with bromine in chloroform to form the rather stable dibromide which boils at 170-174° C. under atmospheric pressure and at 69.5° C. under 24 mm. pressure. Contrary to expectations, this dibromide, unlike the dibromide of cycloheptene, does not combine readily with aliphatic amines. In fact, so stable is it towards dimethylamine that the small amount of 1,4-dibromide of butadiene which is formed with it when it is prepared by the method just described may be separated from it by the action of dimethylamine, which converts it into 1-4-tetramethyldiamino- $\triangle^2$ -butene ($\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{NMe}_2$), which boils at 39-40° C. under 24 mm.

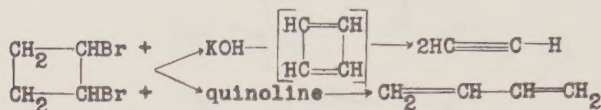
Willstätter and Schmaedel³ used various reagents in an attempt to remove two molecules of hydrogen bromide from 1,2-dibromocyclobutane in order to obtain the theoretically important cyclobutadiene. When the 1,2-dibromocyclobutane was heated with quinoline it gave mainly red condensation products together with a small amount of butadiene. When the dibromide was heated with potassium hydroxide at 100-105° C. 1-bromocyclobutene was obtained, but when it was heated with potassium hydroxide at 200° C. acetylene was formed.

¹Willstatter and Bruce, Ber., 40, 3986 (1907).

²Harries, Ber., 34, 300-304 (1901).

³Willstätter and Schmaedel, Ber., 38, 1994 (1905).

- (1) 1,2-Dibromocyclobutane + quinoline $\xrightarrow{\text{heat}}$ butadiene
- (2) 1,2-Dibromocyclobutane + KOH $\xrightarrow[100^\circ \text{ C.}]{\text{Heat}}$ bromocyclobutene
- (3) 1,2-Dibromocyclobutane + KOH $\xrightarrow[2000^\circ \text{ C.}]{\text{Heat}}$ acetylene

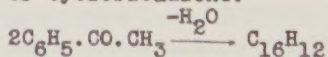


Willstätter and Bruce¹ investigated the action of potassium hydroxide on 1,4-dibromobutene, but in no case did they observe any evidence of ring closure. Their method of procedure may be illustrated by the following equations:

- (1) $\text{CH}_2\text{Br} - \text{CH} = \text{CH} - \text{CH}_2\text{Br} + \text{dry KOH} \longrightarrow \text{CHBr} = \text{CH} - \text{CH} = \text{CH}_2$
- (2) $\text{CHBr} = \text{CH} - \text{CH} = \text{CH}_2 + \text{dry KOH} \longrightarrow 2\text{HC} \equiv \text{C} - \text{H}$

It is thus apparent that every attempt to prepare cyclobutadiene resulted in the formation of acetylene or butadiene. Although Willstätter's results were negative, they are nevertheless important. His investigations in the cyclobutadiene series are significant not only because of the prominence of the investigator but also because of the fact that he has successfully applied these methods to the synthesis of other members of the homologous benzene series, namely, cycloheptatriene and cyclooctatetraene.

Gastaldi and Cherchi² prepared a solid crystalline hydrocarbon melting at 130° C. by heating acetophenone in the presence of sodium ethoxide, and from the manner of its formation and the products given when oxidized they considered it to be the 1,3-diphenyl derivative of cyclobutadiene.



It reacted with sulphuric acid to form a sulphonic acid derivative,

¹Willstätter and Bruce, Ber., **40**, 3979 (1907).

²Gastaldi and Cherchi, Gazz. Chim. Ital., **44**, 282 (1914).

and was oxidized by nitric acid to nitrobenzoic acid. At the time the report was made it created no little interest.¹ By further investigation, however, Gastaldi and Cherchi² proved definitely that the compound which they had described as $C_{16}H_{12}$, 1,3-diphenylcyclobutadiene, was sym-methyldiphenylbenzene, $C_{19}H_{16}$.

The question of the possibility of the existence of cyclobutadiene has also been the subject of a number of theoretical discussions. Crocker³ in a discussion of the "octet" theory and single-ring compounds states that one condition for an aromatic compound is a ring with considerable outward activity strain, so that double bonds are bent outwardly and pairs of extra electrons are forced to the outside of the ring.

"On the basis of this theory rings of three or four members, such as C_2H_2N , C_2H_2O , C_4H_4 , and C_3H_3N , satisfy the requirement for aromatic structure." However, these three- or four-membered rings will be subjected to large disruptive forces due to the repelling action of the atomic kernels. In other words, compounds of this type are hardly expected to exist.

In a more recent study Otto Schmidt⁴ arrives at the same conclusion with regard to the stability of cyclobutadiene. He measured the stability of the cyclic polyolefines $(CH:CH)_n$, by the ratio of the vectorial sum of the affinities R to the radius of the molecule r . For $n = 2$, $R/r = 1.27$; that is, the structure is unstable and cyclobutadiene cannot exist. For $n = 3$, C_6H_6 , $R/r = 0.66$ which is closest to 1 and therefore corresponds to the most stable structure. He calls attention to the fact that attempts to synthesize cyclobutadiene have resulted in the formation of acetylene.

It is a well-known fact that the commonest type of cyclic compounds occurring in nature are those containing five and six carbon atoms. The great difference in behavior between α -, β -, γ -, Δ - hydroxy-acids, as regards the readiness with which they

¹Brooks, "The Non Benzenoid Hydrocarbons," The Chemical Catalog Co. (1922), p. 252.

²Gastaldi and Cherchi, Gazz. Chem. Ital., **45**, II, 251-75 (1915).

³Crocker, J. Am. Chem. Soc., **44**, 1629 (1922).

⁴Otto Schmidt, Ber., **67B**, 2078-80 (1934).

form lactones, and of corresponding dicarboxylic acid as regards the formation of anhydrides is also noteworthy. Many reactions that lead to the formation of five or six atom rings fail when it is attempted to apply these same methods to the production of smaller ring structures. To account for difference in behavior of compounds of this type as well as the differences in the graded stability of the cycloparaffins and their derivatives, Baeyer¹ proposed his strain theory which is based upon a planar configuration. He reasoned on the basis of van't Hoff's assumption that the angle formed by the mutual union of the valencies of any two carbon atoms must be $109^{\circ}28'$. Any distortion of these valency directions will lead to a strain which will result in the loss of stability, and the greater the strain the greater the instability. Ethylene was regarded by Baeyer as the first member of the cyclic series in which the position of the two bonds uniting the carbon atoms must be deflected through an angle of $\frac{109^{\circ}28'}{2}$ so as to form parallel lines between the atoms.

The deflections calculated by Baeyer² which were regarded by him as measures of the strains in the molecules are as follows:

54°44'	cycloethane
24°44'	cyclopropane
9°44'	cyclobutane
0.44'	cyclopentane
-5.16'	cyclohexane
-9°33'	cycloheptane
-12 51'	cyclooctane

According to this conception the cyclopentane ring should be most stable and the cycloethane ring least stable. The relative stabilities of the cycloparaffins should increase up to cyclopentane and then decrease again. Baeyer's theory has been helpful in a qualitative way but the work of Willstätter³ (synthesis of cyclooctatetraene which according to Baeyer's theory should be unstable) and the more recent work of Ruzicka⁴ show that the theory in its original form is untenable. Large strainless rings have been found in nature and many of them have been

¹Baeyer, Ber., 18, 2278 (1885).

²Ibid.

³Willstätter and Waser, Ber., 44, 3424 (1911).

⁴Ruzicka, Bull. Soc. Chem., IV, 43, 1145-73 (1928).

synthesized by Ruzicka.¹ Some compounds may have rings containing as many as thirty-two carbon atoms. It is generally believed that the atoms of these rings do not lie in the same plane.²

A very serious objection to Baeyer's theory was due to the fact that the relative heats of formation of the cyclo-paraffins as determined by Stohman and Kleber³ did not agree with calculations made on the basis of the strain theory. The value obtained for the heat of formation of ethylene was especially out of line.

True enough the contributions made by Ingold and collaborators⁴ brought Baeyer's theory into better agreement with experimentally determined facts but left much to be desired. They suggested that the angle between adjacent valencies will be $109^{\circ}28'$ only when the same atoms or groups are attached to all the four bonds of the carbon atom. From their numerous experimental investigations it seems that the nature of the substituents might have a considerable effect on the valency deflection and hence on the stability of the compounds involved.

The preparation of cyclo-octatetraene by Willstätter and Waser⁵ not only helped to show that Baeyer's theory in its original form was untenable but also called attention to the limitations of another important theory, namely, Thielé's theory,⁶ particularly as it applies to benzene. Thielé's modification of the Kekulé formula⁷ of benzene is written

¹Ruzicka and Stoll, Helv. Chim. Acta, 11, 1159-73 (1928); Ruzicka, Stoll, and Schinz, ibid., 1174-80 (1928).

²Sachse, Ber., 23, 1363 (1890); Zeit Physik. Chem., 10, (1892).

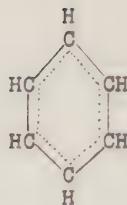
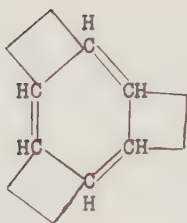
³Stohman and Kleber, J. Prakt. Chemie, 23, 45, 475-99 (1892).

⁴Beasley, Ingold, and Thrope, J. Chem. Soc., 107, 1080-1106 (1915); Ingold and Thrope, ibid., 115, 320-83 (1919); Ingold, ibid., 119, 305-29 (1921). See also "Theories of Organic Chemistry" by Henrich (translated by Johnson and Hahn) (1922), p. 18.

⁵Willstätter and Waser, Ber., 44, 3424 (1911).

⁶Thielé, Ann., 306, 87 (1899). For excellent discussion of Thielé's theory see J. B. Cohen, "Organic Chemistry," Longmans, Green and Co., New York, 1928, Part I, p. 145.

⁷Thielé, Ann., 306, 125 (1899).



Since the molecule is represented as symmetrical and all partial valencies are conjugated, they should differ in no respect from the three linkages represented by single bonds and conjugated residual valencies. Since benzene lacks free residual affinity it should according to this theory behave as a saturated compound. It gives no isomeric ortho-di-substituted compounds because the molecule is perfectly symmetrical. Kekulé¹ assumed the oscillation of double bonds in order to harmonize his formula with the fact that such isomers have not been isolated. It is of interest to note that the results of modern mechanics and X-ray studies by Pauling² and Mack³ seem to confirm Kekulé's hypothesis. The modern terminology for oscillations of conjugated double bonds is resonance. Levine and Cole⁴ have brought further evidence for the Kekulé structure of benzene by the ozonization of o-xylene in which they isolated oxidation products corresponding to both forms of o-xylene in equilibrium. An examination of the structure for cyclo-octatetraene reveals that it differs from benzene in having four instead of three systems of conjugated double bonds. It is a closed conjugated system. It would therefore be expected to be similar in chemical behavior to benzene if it is assumed that it has a planar configuration as required by Baeyer's theory in its original form, but as a matter of fact cyclo-octatetraene stands in marked contrast to benzene. It is a typical olefine. Willstätter states:⁵

¹Kekule, Ann., 162, 86 (1872).

²Pauling, J. Am. Chem. Soc., 53, 1367 (1931).

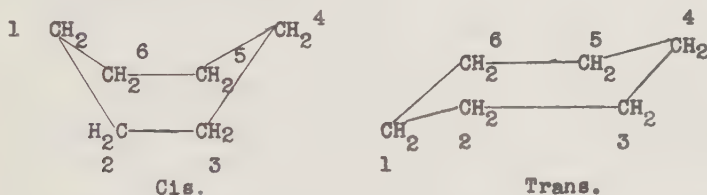
³Mack, J. Am. Chem. Soc., 54, 2141-65 (1932).

⁴Levine and Cole, J. Am. Chem. Soc., 54, 338 (1932).

⁵Willstätter, Ber., 44, 3428 (1911).

Cyclo-octatetraene is absolutely different from benzene in its chemical properties. That it must be regarded as a true olefine follows from the facts: (1) that it readily adds 4 molecules of hydrogen in the presence of platinum as a catalyst while benzene is unreactive under the same conditions; (2) that it instantly reduces potassium permanganate and adds bromine; (3) that it does not readily form substitution products and does not react with nitric acid to give nitro-derivatives, and (4) that it is unstable and tends to rearrange into more stable isomers.

In 1890 Sachse¹ suggested that if in the case of those ring compounds from cyclohexane upwards it is assumed that the carbon atoms take up a multiplanar configuration all strain might be avoided, since the natural angle of the carbon atoms is not strained to equal the angle of a large plane polygon. This idea was subsequently developed by Mohr.² The suggestion of strainless rings led to the further assumption that such molecules might exist in two or more stereoisomeric forms. Theoretically cyclohexane, for example, should exist in two stereoisomeric forms which can be shown by models.



Carbon atoms 2,3,5,6 lie in one plane while atoms 1,4 can lie both in one plane (cis) or each in a separate plane (trans) one above and one below the plane of the four carbon atoms (2,3,5,6). Such isomerism has never been observed.³ However, it was pointed out by Mohr⁴ that the fact that this type of isomerism so far as is known is not exhibited by cyclohexane may be attributed to the readiness with which the two forms are interconvertible.

The investigations of Windaus, Hückel, and Revere⁵, have

¹H. Sachse, Ber., 23, 1363 (1890); Zeit. Physik. Chem., 10, 203 (1892).

²Mohr, J. Prakt. Chem., 98, 315 (1918).

³Wightman, Trans. Chem. Soc., 2541 (1926).

⁴Mohr, J. Prakt. Chem., 98, 315 (1918).

⁵Windaus, Hückel, and Revere⁵, Ber., 56, 91 (1923).

been attended with greater success. These investigators discovered two hexahydrohomophthalic anhydrides. It is clear that if the cyclohexane ring in hexahydrohomophthalic acid is planar, the two carboxyl groups in the trans acid are far apart, but if the ring carbon atom of the $>\text{CH}.\text{COOH}$ or $>\text{CH}.\text{CH}_2.\text{COOH}$ group swings into a strainless configuration, the two carboxyl radicals are brought into such a favorable position that the trans- is more stable than the cis-anhydride. It was also pointed out by Mohr¹ that if two such rings are condensed together as in decahydronaphthalene two stable isomerides should exist. The existence of stable cis- and trans-forms of dicyclic structures are established by the results of Hückel's work on decalane (decahydronaphthalene) and its derivatives. He subsequently obtained all four decahydro β -naphthols, which gave different decahydronaphthalenes on reduction.

It was also indicated by Sachse³ that a study of heats of combustion of the cycloparaffins would provide a clue to their relative strain. A study for the lower rings up to cycloheptane was made by Hückel.⁴ Ruzicka and Schläpfer⁵ made such a study for rings of 8, 15, 17, and 30 carbon atoms. They found the heats of combustion to be in agreement with the Sachse-Mohr theory. Their work indicated that there is a strain in the smaller rings which disappears in the larger rings. According to Perkin⁶ Baeyer's strain theory is truer for small rings, in which there is a positive angular deviation, than for large rings, in which on the basis of the theory there is a negative deviation.

Chemical evidence indicates that the carbon and hydrogen atoms of benzene must lie in a single plane. The study of the crystal structure of hexamethylbenzene substantiates this point. Thus on the basis of the Sachse-Mohr theory one would expect benzene in which the carbon atoms are coplanar to exhibit different chemical properties from its higher homologue cyclooctatetraene

¹Mohr, J. Prakt. Chem., **98**, 315 (1918).

²W. Hückel, Ann., **451**, 109, 132 (1926); Hückel and Stepf, Ann., **163** (1927).

³Sachse, Ber., **23**, 1363 (1890).

⁴Hückel, Ber., **53**, 1277 (1920).

⁵Ruzicka and Schläpfer, Helv. Chim. Acta., **16**, 162-68 (1933).

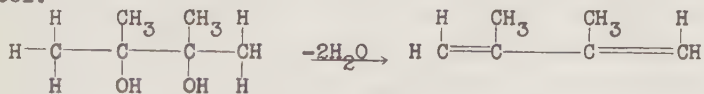
⁶Perkin, Ber., **35**, 2105 (1902).

in which the atoms may take up a multiplanar configuration.

Beginning in 1929 and extending through 1934 Muskat and his students¹ in this laboratory have investigated the characteristic properties and addition reactions of many conjugated compounds. They have studied the addition reactions of phenyl-butadiene, butadiene, carboxybutadiene, chloro- and bromobutadiene and 1-phenyl-4-amino-butadiene. Muskat and Northrup² developed a theory "which explains the addition to conjugated systems without recourse to any special hypothesis of conjugation. Conjugated systems differ from non-conjugated systems only insofar as the former may exhibit α,γ -rearrangement while the latter cannot exhibit this phenomenon."

This investigation, which is a continuation of the study of conjugated systems, had for its objective the preparation of 1,2-dimethylcyclobutadiene. An examination of its structure reveals that it differs from the corresponding benzene derivative in having two instead of three conjugated systems of double bonds. It is a "closed" conjugated system (Thielé ring). It might be thought that this similarity in structure with benzene would lead to similarity in chemical behavior. This, however, was not true in the case of cyclooctatetraene, which was shown by Willstätter³ to be a highly unsaturated compound. Thus it can be seen that the synthesis of 1,2-dimethylcyclobutadiene would be of great interest. Although the parent substance has been shown to be unstable, it does not necessarily follow that all of its derivatives will be unstable.

The general procedure for the preparation of the cyclobutadiene derivative may be briefly outlined as follows: 2,3-dimethylbutadiene was prepared in the usual manner by dehydration of pinacol.

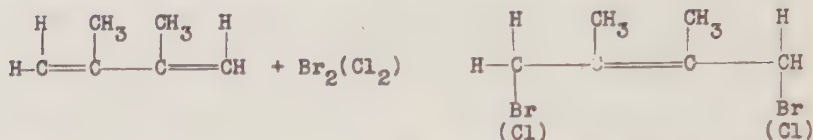


¹Muskat and collaborators, *J. Am. Chem. Soc.*, **51**, 2496 (1929); **52**, 326, 812, 1574 (1930); **53**, 3178 (1931); **55**, 2140 (1933); **55**, 2860 (1933); *Ber.*, **64**, 2860 (1933).

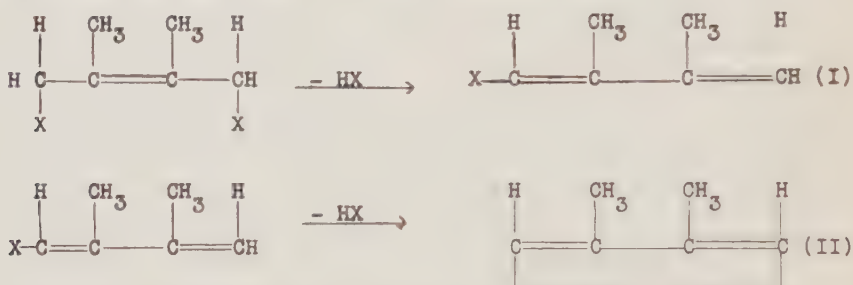
²Muskat and Northrup, *J. Am. Chem. Soc.*, **52**, 4043 (1930).

³Willstätter and Waser, *Ber.*, **44**, 3424 (1911).

The purified dimethylbutadiene was treated with just enough chlorine or bromine to form the dichloride or dibromide, which was shown in each case to have the 1,4-structure.



The dimethylbutadiene dihalide was then treated with an alkaline reagent to remove HX from the 1,4-positions to form, first, the mono-halogen derivative (I), and then the dimethylcyclobutadiene (II) which was the object of this investigation.



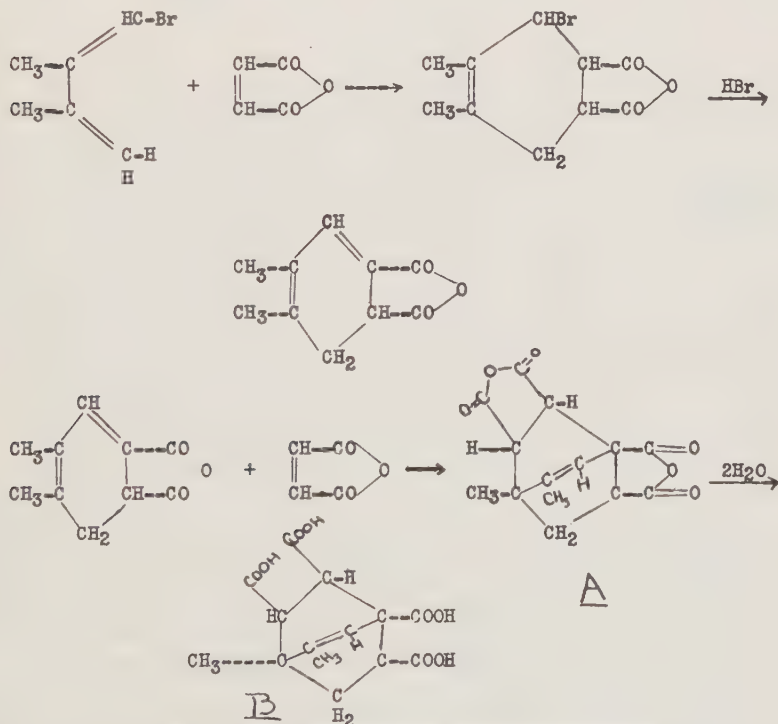
1,4-Dibromo-2,3-dimethylbutene reacted with potassium hydroxide to give (1) 2,3-dimethylbutadiene, identified by its tetrabromide, and its maleic anhydride derivative which was hydrolyzed to the corresponding dicarboxylic acid; (2) some unchanged 1,4-dibromo-2,3-dimethylbutene, identified by its melting point and the melting point of its tetrabromide; (3) 1-bromo-2,3-dimethylbutadiene; and (4) a trace of what is presumably 1,2-dimethylcyclobutadiene, the boiling point 83-84° C. being so close to that of 2,3-dimethylbutadiene that it could not be separated from it by distillation.

Various alkaline reagents were used in place of potassium hydroxide in an attempt to improve the yield of 1-bromo-2,3-dimethylbutadiene; namely, sodium phenolate, alcoholic potash, quinoline, triethanolamine and dimethylaniline. The best results were obtained by the use of dimethylaniline although the yield was not as good as in the case of potassium hydroxide.

The 1-bromo-2,3-dimethylbutadiene was isolated and identified for the first time. It reacts with one molecule of

bromine in carbon disulphide solution to give a stable tribromide which can be distilled under reduced pressure. This tribromide reacts slowly with excess bromine in chloroform or carbon disulphide to give a solid pentabromide melting at 149° C.

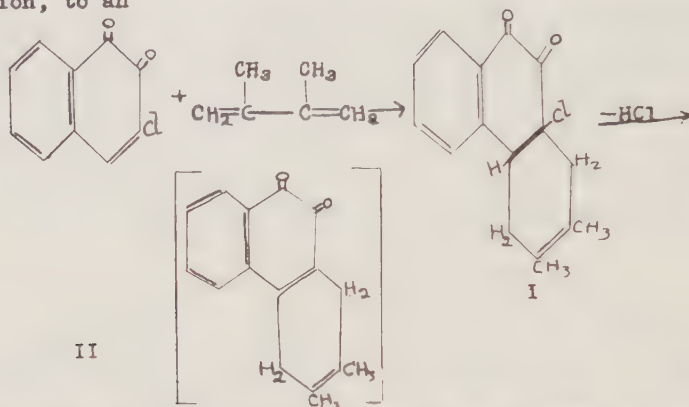
When 1-bromo-2, 3-dimethylbutadiene is treated with a benzene solution of maleic anhydride (Diels and Alder Reaction¹) and the solution heated on a water bath for several hours a crystalline solid separates which is insoluble in alcohol, carbon tetrachloride, chloroform, petroleum ether and in all solvents tried except acetone in which it is slightly soluble. The product contains no bromine and decomposes at about 320° C. without melting. This compound is apparently produced by the reaction of one molecule of 1-bromo-2, 3-dimethylbutadiene with two molecules of maleic anhydride resulting in the loss of one molecule of hydrogen bromide from the intermediate compound



¹Diels and Alder, Ann., 460, 98 (1928); 470, 62 (1929); 478, 139 (1930); Ber., 62, 554, 2081, 2337 (1929).

When the compound A was boiled with water and the solution titrated with standard alkali the results indicated that compound A was converted by hydrolysis into the corresponding tetracarboxylic acid B.

Recently Feiser and Dunn¹ studied the reaction of 2,3-dimethylbutadiene with the 3-chloro- and the 3-bromo-derivatives of ortho-naphtho-quinone. They found that the halogenated ortho-quinones add dimethylbutadiene in chloroform or tetrachloroethane solution, to an

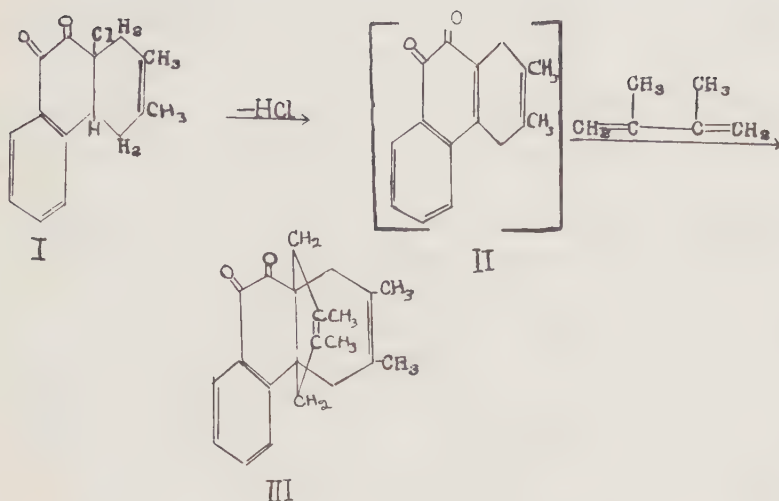


appreciable extent at room temperature and at 100° the reaction is complete in an hour. For the isolation of the product I it was necessary to avoid overheating in the preparation of the material. They found that the pure compound I cannot be kept more than a few hours before decomposition sets in. When the reaction was carried out in excess diene and at temperatures above 100° the reaction product isolated from the solution in 36 per cent yield in a crystalline condition was free from halogen. It had the composition of the chloro-quinone plus two molecules of dimethylbutadiene, less the elements of hydrogen chloride.

Attempts to establish the structure of this product were unsuccessful. However, on the basis of their observations Fieser and Dunn² assumed that "the addition product I, first loses hydrogen chloride from adjacent, bridge carbon atoms, and that the dihydroanthrenequinone II adds a second molecule of the diene at the reactive ethylenic linkage thus established, giving a tetracyclic diketone of structure III."

¹Feiser and Dunn., *J. Am. Chem. Soc.*, **59**, 1021 (1937).

²*Ibid.*



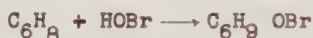
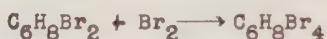
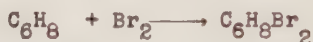
Under similar conditions of experiment, an identical product was obtained from 3-bromo-1,2-naphthoquinone. These observations of Feiser and Dunn¹ that 3-bromo-1,2-naphthoquinone reacts with 2,3-dimethylbutadiene to give the unstable product II are interesting in view of the fact that the writer had observed before Feiser's work was published that the product of the interaction of maleic anhydride and 1-bromo-2,3 dimethylbutadiene readily loses a molecule of hydrogen bromide to form a reactive ethylenic linkage which then reacts with another molecule of maleic anhydride to give a stable compound.

When the 1-bromo-2,3-dimethylbutadiene to which a few crystals of β -naphthol had been added was heated above 154° C. with a large excess of powdered potassium hydroxide under a short column most of it polymerized to a thick rubber-like substance. However, a small quantity of a hydrocarbon possessing a fragrant and characteristic odor distilled over together with water and some unchanged monobromide. After repeated distillations, in the same manner, a small quantity of a hydrocarbon (in many cases only a few drops) was obtained which after being dried over anhydrous calcium sulphate distilled at 83-84° C. under atmospheric pressure. It polymerized to a thick syrupy substance when

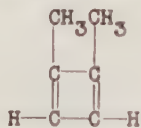
¹Ibid.

allowed to stand for a few hours at room temperature in a test tube. In most cases when it was desired to keep the hydrocarbon for any length of time it was kept in a sealed tube which was suspended in a carbon dioxide-snow bath.

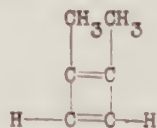
Analysis for carbon and hydrogen and a molecular weight determination indicate that this hydrocarbon has the formula C_6H_8 . It is evident that the effect of the powdered potassium hydroxide is to remove one atom of hydrogen and one atom of bromine from the monobromide, presumably from the 1,4-positions. An examination of this hydrocarbon for chemical properties shows that it is an unsaturated compound. In the absence of light and at a low temperature, it readily absorbs one molecule of bromine to give a liquid tetrabromide, and there is no appreciable amount of hydrogen bromide liberated. Aqueous solutions of potassium permanganate are almost instantly reduced, the brown manganese dioxide appearing in neutral solution.



Several attempts were made to determine the structure of this hydrocarbon by ozonization. It is evident from the method of synthesis and from the reactions involved that the hydrocarbon could be represented by one of the following structures:

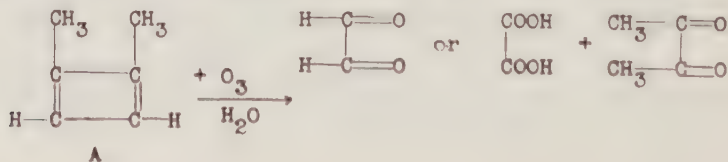


A

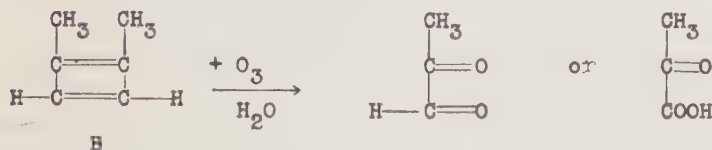


B

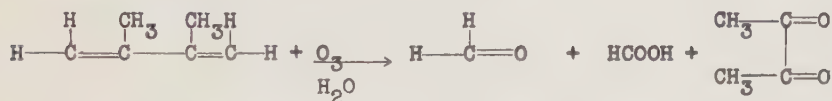
If it has structure A, it would yield on ozonization, followed by hydrolysis glyoxal or oxalic acid, and diacetyl.



If it has structure B, it would yield on ozonization and subsequent hydrolysis pyruvic aldehyde or pyruvic acid.



If the hydrocarbon was contaminated with the original hydrocarbon 2,3-dimethylbutadiene, it would yield on ozonization and subsequent hydrolysis formaldehyde, formic acid, and diacetyl.



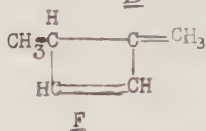
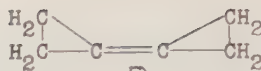
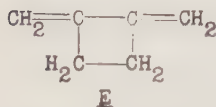
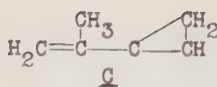
Several samples have been ozonized under varying conditions with different solvents; acetic anhydride, carbon tetrachloride, chloroform, petroleum ether, and ethylchloride were used. Among the methods tried were those used by Muskat and his students;¹ Whitmore and Church,² who made use of the zinc-water-catalyst; and Levine and Cole³ who have shown that when o-xylene is submitted to ozonolysis in various solvents, it gives glyoxal, methylglyoxal and diacetyl, each of which can be isolated in the form of its p-nitrophenylhydrazone or osazone. The p-nitrophenylosazone of diacetyl was obtained and identified by its melting point. The melting point of a mixture with authentic p-nitrophenylosazone of diacetyl was not lowered. No oxalic acid or glyoxal could be detected in any of the various experiments tried. In one ozonization experiment what seemed to be conclusive evidence for the presence of pyruvic acid was obtained. This will be discussed fully in the experimental part.

In addition to the two structures which we have just discussed the hydrocarbon, C₆H₈ might be represented by one of the following structures:

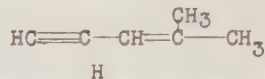
¹Muskat and Huggins, J. Am. Chem. Soc., 51, 2496 (1929).

²Whitmore and Church, J. Am. Chem. Soc., 56, 176 (1934).

³Levine and Cole, J. Am. Chem. Soc., 54, 338 (1932).



If we assume a rearrangement of a methyl group the following are possible:



The synthesis of the hydrocarbon by the action of potassium hydroxide on 1-bromo-2,3-dimethylbutadiene would seem to eliminate the possibility of the compound having structure D. If the compound can be represented by any one of the structures, C, E, F, G, or H, it should yield on ozonization and subsequent hydrolysis one molecule of formaldehyde for each molecule of the substance oxidized. No considerable amount of formaldehyde could have been produced as a result of the ozonolysis since the vapors generated by the hydrolysis of the ozonide and swept by a stream of carbon dioxide into water and into an alcoholic solution of α -naphthol gave no test for formaldehyde. However, when a solution of dimethyl-dihydroresorcinol (methone) was substituted for the α -naphthol and the experiment carried out in the same manner a few crystals, which melted at 186° , the melting point of the dimethone derivative of formaldehyde, were isolated. The melting point of a mixture of this substance with authentic methylene dimethone was not lowered, thus indicating that a trace of formaldehyde was present. While it must be admitted the evidence does not enable one to discriminate conclusively in favor of any one formula, the absence of formaldehyde, except in minute traces, among the fragments of ozonization seems to eliminate structures C, E, F, G, and H.

Chlorination of 2,3-Dimethylbutadiene

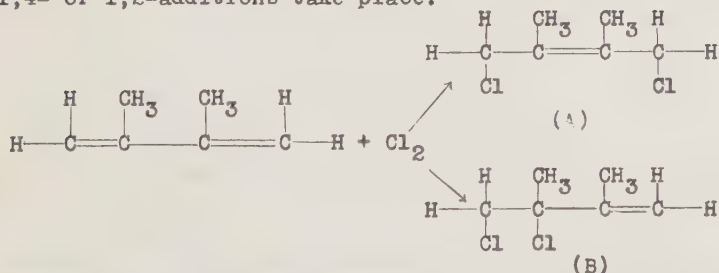
In the course of our investigation with 1,4-dibromo-2,3-dimethylbutene it was thought advisable to study the corresponding chlorine derivative. While much attention has been paid to the addition of chlorine to conjugated systems the action of chlorine on 2,3-dimethylbutadiene has not been reported in the literature. The chlorination of butadiene in non-polar solvents has been investigated by Muskat and Northrup¹ who showed that the

¹Muskat and Northrup, *J. Am. Chem. Soc.*, **52**, 4043 (1930).

product was a mixture of 1,2- and 1,4-dichlorides, boiling points 115° C. and 145° C., respectively, with the two stereoisomeric 1,2,3,4-tetrachlorobutanes; a similar result was obtained at -75° C. in the absence of any solvent. They proved the structure of the dichlorides by ozonization. Muskat and Huggins¹ proved by ozonization that 1-phenylbutadiene reacts with chlorine to form a 3,4-dichloride boiling at 125°C. under 3 mm. Jones and Williams² investigated the action of chlorine on isoprene. They dissolved pure isoprene in carbon tetrachloride and added chlorine (one mol) in the form of a solution in the same solvent, very slowly, the mixture being continuously stirred and cooled. On fractionation of the residue after removal of the solvent they obtained two products which were shown to be 1-chloro-2-methylbutadiene and 1,4-dichloro-2-methyl- $\triangle^2$ -butene. Indications of the presence of a lower boiling point dichloride were obtained. The structure of the dichloride was determined by ozonization.

The 2,3-dimethylbutadiene which had been carefully fractionated and twice distilled over sodium was chlorinated in various solvents under strong cooling in a salt ice-bath. Of the solvents tried—carbon tetrachloride, chloroform, carbon disulphide, and ether—the best results were obtained when ether was used. On fractionation of the residue left after removal of the solvent, two main products were obtained, a compound which was shown to be 1,4-dichloro-2,3-dimethyl- $\triangle^2$ -butene and varying amounts of a chloride distilling at a lower temperature which from the analysis and boiling point was apparently chlorodimethylbutadiene. Its structure is now being investigated.

Two compounds may be derived from 2,3-dimethylbutadiene when it is treated with one mol of chlorine, depending on whether 1,4- or 1,2-additions take place.

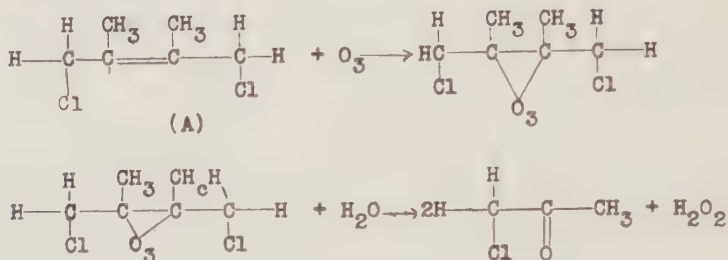


¹Muskat and Huggins, *J. Am. Chem. Soc.*, **51**, 2496 (1929).

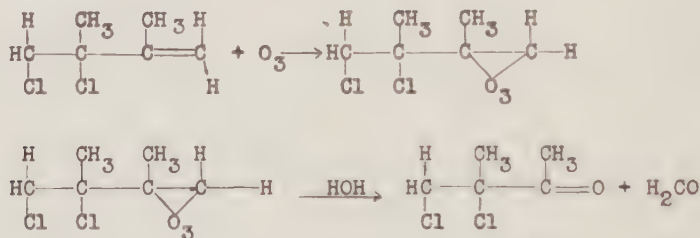
²Jones and Williams, *J. Chem. Soc.*, **828** (1934).

Compound (A) would result from 1,4 addition of chlorine; compound (B) from 1,2 addition.

The structure of the dichloride was determined by ozonization. A dichloride of structure (A) would yield on ozonization and subsequent hydrolysis two molecules of monochloroacetone.



A dichloride of structure (B) would yield on ozonization and subsequent hydrolysis 1,2-dichloro-2, methylbutanone-3, formaldehyde and formic acid.



When a solution of the dichloride (b.p. 77° C. under 10 mm. pressure) in dry carbon-tetrachloride was subjected to ozonization and the ozonide worked up in the usual manner chloroacetone was isolated in the form of its semicarbazone, melting point 153° C. The melting point of a mixture of this semicarbazone with authentic semicarbazone of chloroacetone was 153° C. When a solution of the ozonide to which semicarbazide hydrochloride and sodium acetate had been added was heated for a short time, a semicarbazone of chloroacetone could not be isolated but instead the semicarbazone of pyruvic aldehyde melting at 254° C. was obtained. This means that chloroacetone is very easily converted into acetol in the presence of sodium acetate. This ozonization proves that the stable dichloride is the 1,4-compound (A).

When this dichloride was ozonized and the ozonide decom-

posed in such a manner that the volatile products were swept into an alcoholic solution of β -naphthol a derivative of formaldehyde was not formed. Since this sensitive test for formaldehyde was negative it may be taken as evidence that the 1,2-dichloride was absent. This simply means that the higher, stable dichloride was free from any 1,2-dichloride. It does not exclude the possibility of the existence of an unstable dichloride which decomposed upon distillation with the liberation of hydrogen chloride to form a mono-chloride. In fact the presence of large quantities of what was presumably a monochloride among the chlorination products each time the dichloride was prepared seems to indicate that there may have been an unstable dichloride formed which lost hydrogen chloride when distilled to give monochlorodimethylbutadiene. It is also noteworthy that whenever the chlorination was carried out at temperatures above zero hydrogen chloride was liberated and the corresponding yield of the dichloride was reduced. This indicates that the monochloride is a decomposition product of the 1,4-dichloride of dimethylbutadiene.

Oxidation of the dichloride with neutral potassium permanganate in an acetone solution according to the method of Farmer, Lawrence, and Scott¹ gave a solid which after being crystallized from ether melted at 94° C. Since the dichloride was shown to be 1,4-dichloro-2,3-dimethyl-2-butene this compound was evidently 1,4-dichloro-2,3-dimethyl-2,3-dihydroxybutane. The corresponding dibromhydrin is also known.²

When the dichloride was mixed with twice its weight of dry powdered potassium hydroxide and the mixture heated on an oil bath to 180° a small quantity of a low boiling point chloride distilled through the condenser. This chloride was fractionated and analyzed for chlorine. The analysis indicates that it is monochlorodimethylbutadiene. Its boiling point, 28° C. under 10 mm. pressure, is the same as the boiling point of the mono-chloride obtained in the fractional distillation of the dichloride described above. The low yield of the chloride rendered the process useless for our purpose so we did not determine the structure of the monochloride at this time, however, since it was formed from the

¹Farmer, Lawrence, and Scott, *J. Chem. Soc.*, 521 (1930).

²*Ibid.*, 521 (1930).

1,4-dichloride it seems likely that the monochloride has the structure, 1-chloro-2,3-dimethylbutadiene.



In the course of this investigation the action of chlorine and hypobromous acid on 2,3-dimethylbutadiene has been studied. It has also been demonstrated that the dibromide of 2,3-dimethylbutadiene loses a molecule of hydrogen bromide from the 1,4-positions, to give 1-bromo-2,3-dimethylbutadiene when it is treated with powdered potassium hydroxide or dimethylaniline. This 1-bromo-2,3-dimethylbutadiene reacts further with powdered potassium hydroxide to give a small yield of a hydrocarbon which is presumably 1,2-dimethylcyclobutadiene.

Although entirely satisfactory evidence for the structure of the hydrocarbon which boils at 83° is not available, the analysis, the molecular weight determination, the isolation of diacetyl as one of the products of ozonization, the bromination experiments, indicate that the compound is 1,2-dimethylcyclobutadiene. The hydrocarbon reacts with one mole of bromine to give a dibromide which is clearly a different compound from the dibromide of 2,3-dimethylbutadiene. The dibromide of 2,3-dimethylbutadiene is a sharp-smelling liquid with lachrymatory properties whereas the dibromide of the supposed 1,2-dimethylcyclobutadiene has almost no lachrymatory properties. This dibromide reacts with another molecule of bromine to form a liquid tetrabromide which is fairly soluble in ligroin. The tetrabromide of 2,3-dimethylbutadiene is a crystalline solid almost insoluble in ligroin. The fact that only a trace of formaldehyde could be detected among the fragments of ozonization seems to indicate that no considerable amount of 2,3-dimethylbutadiene could have been present, since no difficulty whatever has been encountered in isolating derivatives of formaldehyde when dimethylbutadiene has been ozonized as a control. Also in one experiment, the hydrocarbon was heated with maleic anhydride in benzene solution. After standing several days an amorphous solid separated which could not be crystallized. Under similar conditions 2,3-dimethylbutadiene yielded crystalline needles after standing for a few minutes. On the other hand, if the compound is 1,2-dimethylcyclobutadiene it is difficult to explain the fact that in the many ozonization experiments that

have been carried out not even a trace of glyoxal or its oxidation product, oxalic acid, has been isolated. Before the structure can be definitely established as that of the cyclic compound glyoxal or pyruvic acid must be isolated among the oxidation products.

If it is assumed that the hydrocarbon is a cyclobutadiene derivative, then our work demonstrates that a cyclic compound, containing two double bonds in conjugation capable of oscillation, does not have aromatic properties, and is in accordance with the results obtained by Willstätter with cyclooctatetraene. It must, therefore, mean that the properties of benzene, which distinguishes it from other cyclic compounds, are characteristic not only of its conjugated double bonds, capable of cyclic oscillation as Thielé would have it, but it appears to be specific for the C_6 cyclic compounds.

II. EXPERIMENTAL

Preparation of 2,3-Dimethylbutadiene.—Acetone was reduced to pinacol hydrate by a procedure described in "Organic Syntheses."¹ This method used is a slight modification of a procedure given by Hollemann,² and the hydrate was converted into anhydrous pinacol by distillation under reduced pressure. Of the procedures tried for converting the pinacol into 2,3-dimethylbutadiene the catalytic dehydration with hydrobromic acid or aniline hydrobromide (method of Kyriadides³) gave best results. It was very thoroughly washed, dried over calcium chloride and fractionated; after a final distillation over sodium, according to the method of Farmer, Lawrence, and Scott,⁴ it distilled at 69-70° C. under atmospheric pressure. The yield was about 60 per cent of

¹Carl Marvel, "Organic Syntheses," John Wiley & Sons, New York, 1925, Vol. V, p. 87.

²Hollemann, Rec. Trav. Chim., **25**, 206 (1906).

³Kyriadides, J. Am. Chem. Soc., **36**, 987 (1914).

⁴Farmer, Lawrence, and Scott, J. Chem. Soc., 512 (1930).

the theoretical. Distillation of the pinacol in an Anschutz flask over 10 per cent of potash alum¹ gave good yields of the diene, but not quite as good as distillation with a trace of hydrobromic acid or aniline hydrobromide.

Bromination of 2,3-Dimethylbutadiene.—The bromination of 2,3-dimethylbutadiene has been extensively investigated.² The method used here is that of Macallum and Whitby³ slightly modified by Farmer, Lawrence, and Scott.⁴

The 2,3-dimethylbutadiene purified in the manner described above was brominated at 0° C. in carbon tetrachloride, petroleum ether, or chloroform solution; the solvent was removed in vacuo and the dibromide distilled under reduced pressure. The product distilling 105–110° C. under 18 mm. pressure was used in most of the experiments that follow. In agreement with Kondakov⁵ both a liquid and a solid form of the dibromide of 2,3-dimethylbutadiene were obtained. The solid was obtained free from the liquid isomer by repeated crystallizations from methyl alcohol. It melted at 47° C., the melting point reported in the literature for the dibromide. In most cases no attempt was made to separate the two isomers since it was soon discovered that both forms gave the same monobromide when treated with powdered potassium hydroxide or dimethylaniline. Macallum and Whitby⁶ assumed that the liquid like the solid is a 1,4-compound and attempted to decide which was the cis and which the trans form by causing reaction to take place with dimethylamine. Farmer,⁷ however, contends that the results obtained by Macallum and Whitby failed to prove the existence of cis-trans isomerism in these compounds. The chief difficulty lies

¹Macallum and Whitby, trans. Roy. Soc. Canada, 22, III, 33 (1928).

²Maruiza, J. Russ. Phys. Chem., 21, 434 (1889); Couturier, Ann. Chem., 26, 480 (1892); Knodakov, J. Prakt. Chem., 62, 166 (1900); Courtot, Bull. Soc. Chem., 35, 949 (1906).

³Macallum and Whitby, trans. Roy. Soc. Canada, 22 (III), 33 (1928).

⁴Farmer, Lawrence, and Scott, J. Chem. Soc., 512 (1930).

⁵Kondakov, J. Prakt. Chem., 62, 166 (1900).

⁶Macallum and Whitby, trans. Roy. Soc. Canada, 22, III, 33 (1928).

⁷Farmer, Lawrence, and Scott, J. Chem. Soc., 512 (1930).

in the fact that no one thus far has ever had any of the liquid isomer free from the corresponding solid.

Preparation of 1-Bromo-2,3-Dimethylbutadiene by the Action of Potassium Hydroxide on 1,4-Dibromo-2,3-Dimethylbutene.—

Powdered potassium hydroxide (200 grams) was placed in a dry Kjeldahl flask, and to this was quickly added 100 grams of freshly distilled 1,4-dibromo-2,3-dimethylbutene. The flask was stoppered and the contents thoroughly mixed by shaking. The flask was connected by a wide bent glass tube to an efficient condenser, which was provided with an adapter leading into a 500 cc. filter flask immersed in an ice bath.

The mixture warmed up and the flask was immediately plunged into an oil bath previously heated to 154° C. The temperature was kept between 154 and 165° C. and the mixture was shaken occasionally. Heat was applied until vigorous ebullition occurred, whereupon a spontaneous distillation of the reaction mixture took place. When the reaction slackened, the flask was heated as before. The mass, which became brownish in color as the volatile components were removed, was heated until no more liquid distilled. In the initial vigorous ebullition, most of the material distilled during a few minutes, and it was necessary to wait until this reaction was over before continuing to heat the flask. Otherwise large quantities of the dibromide distilled over with the other products. The distillate was transferred to a separatory funnel, taken up with ether and the ethereal extract washed several times with water, dried first over calcium chloride and finally over anhydrous calcium sulphate (Drierite).

The ethereal solution containing a mixture of some unchanged 1,4-dibromide, a brownish colored polymer, 2,3-dimethylbutadiene, and a trace of hydrocarbon having a characteristic fragrant odor was poured into a distilling flask connected to a condenser. The flask was heated on a water bath until the ether and the hydrocarbons were distilled off. The residue in the flask was distilled under reduced pressure. Most of it distilled at 55° C. under 20 mm. pressure. Yield 11 to 12 grams or 18 per cent of the theoretical. There remained in the flask the dibromide and a thick polymer.

A portion of the distillate boiling at 55° C. under 20 mm. pressure was analyzed for bromine.

Anal. Subs., 0.2282, 0.2361: AgBr, 0.2382, 0.2467.
Calcd. for $C_6H_{11}OBr$: Br, 44.82. Found: Br, 44.42, 44.48.

It was found that whenever the product was analyzed for bromine immediately after distillation the percentage of bromine found was near that required for the theoretically possible bromhydrin of 2,3-dimethylbutadiene. This led to the belief that an hydroxyl group had been substituted for one of the bromine atoms, leading to the formation of 1,-bromo-4 hydroxy-2,3-dimethylbutene.

It was decided to synthesize the bromhydrin by the action of hypobromous acid on 2,3-dimethylbutadiene. Directions for its synthesis are given below. It distils at $62-64^{\circ}$ C. under 3.4 mm. pressure. The boiling point clearly indicates that it is a different compound from the one obtained by treating the dibromide with potassium hydroxide. Also no satisfactory test for the presence of the hydroxyl group could be obtained from the supposed bromhydrin obtained from potassium hydroxide treatment. It did not react with acetyl chloride, benzoyl chloride or phosphorus tribromide. These reagents caused some of the bromide to polymerize. The remainder could be recovered unchanged. Carbon and hydrogen analysis invariably gave results that were too high for the bromhydrin. Finally it was discovered that when this bromine-containing liquid was dissolved in ether and kept over anhydrous calcium sulphate for two weeks and finally distilled through an 18 cm. column under reduced pressure, subsequent analysis indicated that it was 1-bromo-2,3-dimethylbutadiene. It distilled at 35° under 7 mm. pressure. Apparently the original distillate was a mixture of the monobromide and a hydrocarbon distilling at about the same temperature, and that when the hydrocarbon was allowed to polymerize, the monobromide could be obtained pure.

Preparation of 1-Bromo-2,3-Dimethylbutadiene by Heating 1,4-Dibromo-2,3-Dimethylbutene with Dimethylaniline.—In a 500 cc. Kjeldahl flask was placed 50 grams of 1,4-dibromo-2,3-dimethylbutene and 26 grams of freshly distilled dimethylaniline. The flask was thoroughly shaken, after which it was connected by a wide bent tube to a condenser, which was provided with an adapter leading into a 500 cc. receiving flask immersed in a salt ice bath. The mixture was allowed to stand for at least thirty minutes at room temperature, until the entire mass became solid. The Kjeldahl flask was rapidly heated in an oil bath until a thermometer placed

in the bath indicated that the temperature was 155° C. whereupon a vigorous reaction occurred. The flame was removed until the reaction subsided, after which the flask was heated as long as anything distilled over.

The distillate was taken up with ether, washed several times with dilute sulphuric acid and then with water, dried over calcium chloride and then over calcium sulphate. The ether was removed in vacuo, and the mono-bromide distilled through an 18 cm. column under reduced pressure. It distilled at 35° C. under 7 mm. pressure indicating that it is the same compound obtained by the action of potassium hydroxide on 1,4-dibromo-2,3-dimethyl-butene. The mono-bromide obtained by this method was found to be easily purified. However, the yield obtained (5 gm.) 16 per cent of the theoretical, was smaller than that obtained by the potassium hydroxide treatment. Most of the material polymerised to a thick viscous mass which remained in the Kjeldahl flask.

Anal. Calcd. for C_6H_9Br : Br, 49.68; C, 44.72; H, 5.60;
mol. wt., 161.

Found: Br, 49.53, 49.50; C, 44.62, 45.11; H, 5.75,
5.54. Found mol. wt. 163, 161.5 (cryoscopic method).

Preparation of 1-Bromo-4-Hydroxy-2,3-Dimethyl- Δ^2 -Butene.—The method of Walker¹ was used. 2,3-Dimethylbutadiene (26.g.) was dissolved in 300 cc. of ether in a three liter round bottom flask which contained a solution of sodium bicarbonate. The flask was put in a salt ice bath and the mixture stirred vigorously with a mechanical stirrer. A solution of sodium hypobromite (calculated for 1 mol) was added drop-wise. The mixture was allowed to stand over night, after which the ethereal layer was removed, dried over sodium sulphate and finally over anhydrous calcium sulphate. The ether was removed in vacuo and the residual oil distilled under reduced pressure. The colorless liquid distilled at 62-65° C. under 3.5 mm. pressure. Yield 40 to 50 per cent of the theoretical. A residue remained in the flask.

Anal.: Calcd. for $C_6H_{11}OBr$: Br, 44.84; C, 40.22; H, 6.14.
Found: Br, 44.90, 44.72; C, 40.19, 40.16; H, 6.12, 6.17.

The bromhydrin (2 g.) was dissolved in carbon tetrachloride and a current of ozonized oxygen was bubbled through the solution for twelve hours. An ozonizer similar to the one described

¹Walker, U. S. Pat. 972, 952; ibid., 972, 954.

by Henne¹ was used. A 3 to 4 per cent ozone concentration was used in these experiments. After the ozonization was completed the solvent was removed in vacuo and the viscous ozonide was decomposed with water. To assure complete decomposition the ozonide was heated for two hours on a water bath. Bromo-acetone identified by the melting point of its semicarbozone, 143° C., was isolated. The yield of the semicarbozone (1.82 g.) was 66.5 per cent of the theoretical. A phenylosazone of methylglyoxal melting at 145° was also isolated in 60 per cent yield. This proved that the bromhydrin was a 1,4-addition compound and had the structure, 1-bromo-4-hydroxy-2,3-dimethyl-²butene.

Maleic Anhydride Derivative of 1-Bromo-2,3-Dimethyl-Butadiene.—Maleic anhydride (2 g.) and mono-bromide (3.2 g.) were dissolved in thiophene-free benzene and refluxed together for 24 hours; the crystals obtained on cooling were washed with alcohol, and finally with ether. It was insoluble in all solvents tried except acetone from which it could be crystallized, a large volume of acetone being required. It decomposed above 320° C.

Anal.: Calcd. for $C_{14}H_{12}O_6$; C, 60.87; H, 4.38, Mol. Wt. 276
Found: C, 60.84, 60.41; H, 4.32, 4.58; Mol. Wt., 286
(Rast method).

Two samples of the maleic anhydride derivative were weighed and hydrolyzed to the corresponding acid. The resulting acid solutions were titrated with a tenth normal solution of sodium hydroxide using phenolphthalein as indicator.

Anal. Subs. 0.1728, 0.2815: 0.1087 N. Alkali 19.97⁰⁰., 33.6⁰⁰.
Neutralization equivalent, Calcd. for $C_{14}H_{15}O_8$ 78.09.
Found: 76.9, 77.08.

The results indicate that the anhydride is hydrolyzed to the corresponding tetracarboxylic acid.

Reaction of 1-Bromo-2,3-Dimethylbutadiene with Bromine.—The monobromide was dissolved in carbon disulphide and a solution of bromine (calcd. for 1 mol) in the same solvent was added under strong cooling with constant stirring. After the solvent was removed the residue, a pale yellow oil, was distilled under reduced

¹Henne, J. Amer. Chem. Soc., 51, 2676 (1929).

pressure. It distilled at 104-105° C. under 3 mm. pressure. Yield 85 to 95 per cent.

Anal.: Calcd. for $C_6H_9Br_3$; Br, 74.7; C, 22.24; H, 2.84

Found: Br, 74.72, 74.60; C, 22.28, 22.47; H, 3.01, 3.10.

1-Bromo-2,3-dimethylbutadiene (5 g.) was dissolved in carbon disulphide and a large excess of bromine was added to the cold solution. It was placed in the dark and allowed to stand for several days. A solid separated which melted at 149.5° C. Analysis indicated that it was a pentabromide. Yield 90 to 95 per cent.

Anal.: Calcd. for $C_6H_9Br_5$: Br, 83.16; Found: Br. 83.30, 83.49.

These experiments indicate that 1,4-dibromo-2,3-dimethylbutene loses one molecule of hydrogen bromide from the 1,4 positions to give 1-bromo-2,3-dimethylbutadiene when it is heated with potassium hydroxide or dimethylaniline.

Isolation of 2,3-Dimethylbutadiene.—That portion of the distillate boiling below 85°, obtained in the preparation of 1-bromo-2,3-dimethylbutadiene¹ by the action of potassium hydroxide on 1,4-dibromo-2,3-dimethylbutene, was washed several times with water and dried over calcium chloride. It was then fractionated several times and twice distilled over sodium. It distilled at 69° under atmospheric pressure. The boiling point and analysis indicate that the compound is 2,3-dimethylbutadiene. The yield varied (3.31 to 5.5) 10 to 15 per cent of the theoretical.

Anal.: Calcd. for C_6H_{10} ; C, 87.80; H, 12.20; Found; C, 87.72, 87.63; H, 12.0, 12.30.

The hydrocarbon (1.5 g.) boiling at 69° C. was dissolved in 10 ml. of benzene solution containing maleic anhydride (2 g.) and kept at room temperature for 24 hours. A good yield of crystal separated, 95 to 100 per cent of the theoretical. It crystallized from petroleum ether (B.p. 60-80° C.) in colorless needles melting at 78° C. The melting point of mixture with authentic 4,5-dimethyl-cis- Δ^4 -tetra-hydrophthalic anhydride was 78° C.

When this compound was heated for a few minutes with a

¹See page 25.

little water the anhydride yielded 4,5-dimethyl-cis-4-tetrahydrophthalic acid which separated from the aqueous liquor. After crystallization from alcohol, it melted at 186-190° C. The melting point of a mixture with the authentic compound was 186-190° C.

The hydrocarbon boiling at 69° C. was dissolved in carbon tetrachloride and to this was added a solution of bromine in the same solvent. The solvent was removed under reduced pressure and the product recrystallized from petroleum ether. The crystals melted at 137° C. the melting point of tetrabromo-2,3-dimethylbutane. The melting point of a mixture of this bromide with authentic tetrabromide prepared from pure 2,3-dimethylbutadiene was 137° C.

Anal.: Calcd. for $C_6H_{10}Br_4$; Br, 79.60 Found: Br, 79.83, 80.06.

This proves that a portion of the 1,4-dibromo-2,3-dimethylbutene loses a molecule of bromine from the 1,4-positions when heated with powdered potassium hydroxide to form the original hydrocarbon.

1,2-Dimethylcyclobutadiene.—The hydrocarbon was prepared by treating 1-bromo-2,3-dimethylbutadiene (33 gm.) to which a little naphthol had been added with very dry powdered potassium hydroxide and allowing the mixture to stand at room temperature for thirty minutes. The reaction mixture was then heated at 154-165° C. in an oil bath. A mixture of hydrocarbon and monobromide distilled over when the oil bath reached 154° C. The distillate was dried over calcium sulphate and again heated with potassium hydroxide. The process was repeated until the distillate no longer gave a test for bromine. This usually required four or five distillations. The hydrocarbon, a clear liquid having a fragrant and characteristic odor, distilled at 82-83° C. It polymerizes readily to a thick syrupy liquid unless kept in a carbon dioxide snow bath. The yield was low, varying from 3 to 6 per cent. The largest amount of hydrocarbon obtained at any one time was 2.5 grams, which was prepared from 165 grams of 1-bromo-2,3-dimethylbutadiene.

The hydrocarbon was analyzed for carbon and hydrogen:

Anal.: Subs., 0.1957, 0.0950; CO_2 , 0.6476, 0.3067;
 H_2O , 0.1808, 0.0845. Calcd. for C_6H_8 ; C, 90;
H, 10; Found: C, 90.28, 89.94; H, 10.33, 10.17.

Determination of the molecular weight by the Victor
Meyer Method gave the following results:

Subs., 0.0581, 0.1113 gm.: Vol. 18.4 cc. (25.4° and
732.1 mm.)
Vol. 36.3 cc. (28° and 732.5 mm.); Calcd. for C_6H_8 :
Mol. Wt. 80. Found: Mol. wt., 82.54, 81.71.

Reaction of Bromine with the Hydrocarbon.—A small
sample of the hydrocarbon was dissolved in dry chloroform and to
this solution was added a solution of bromine in the same solvent
under strong cooling in a salt ice bath. The solvent was removed
in vacuo. The residue, a thick oil, was analyzed for bromine.
Yield 95-100 per cent.

Anal.: Subs., 0.4211 gm.; 0.0788 gm.; AgBr, 0.7858,
0.5198.
Found: Br, 79.76, 79.54. Calcd. for $\text{C}_6\text{H}_8\text{Br}_4$: Br, 80.

Another sample was analyzed for carbon and hydrogen.
Anal.: Subs., 0.0891 gm.; 0.0876 gm.; CO_2 0.0580.
0.0576; H_2O , 0.0167, 0.0164. Found: C, 17.74, 18.27;
H, 2.097, 2.09. Calcd. for $\text{C}_6\text{H}_8\text{Br}_4$: C, 18; H, 2.00.

The hydrocarbon also forms a dibromide which distills
under 7 mm. without decomposing. The boiling point could not be
determined because of the small size of the sample. Only 42 per
cent of the theoretical weight of the dibromide was recovered.

Anal.: Subs., 0.0927 gm., 0.1316 gm., AgBr, 0.1456,
0.2199. Found: Br, 66.84, 66.57. Calcd. for $\text{C}_6\text{H}_8\text{Br}_2$:
Br, 66.66.

The hypobromous Derivative of the Hydrocarbon.—One gram
of the hydrocarbon was treated with an aqueous solution of hypo-
bromous acid according to the method of A. W. Francis.¹ The
hydrocarbon was added to the solution of hypobromous acid calcu-
lated for 1 mol and after vigorous shaking at definite intervals
for one hour it was allowed to stand over night at room tempera-
ture. The reaction mixture was extracted with ether. The

¹A. W. Francis, J. Am. Chem. Soc., 47, 2342 (1925).

ethereal extract was washed with water and dried first over anhydrous sodium sulphate and finally over anhydrous calcium sulphate. This solution was filtered and the ether removed in vacuo. It was analyzed for bromine. Yield quantitative.

Anal.: Subs., 0.1460 gm.; AgBr, 0.1568, Found:
Br, 45.81. Calcd. for C_6H_9OBr ; Br, 45.20.

Ozonization of 1,2-Dimethylcyclobutadiene.—A sample of the hydrocarbon boiling at 83-84° C. was dissolved in dry carbon tetrachloride and a stream of ozonized oxygen passed through the solution for twelve hours. The temperature was maintained at 0° C. throughout the entire period of ozonization. After the ozonization was completed the solvent was removed under reduced pressure. Fifty cc. of water was added to the ozonized product and the mixture allowed to stand at room temperature for two hours. To insure complete decomposition of the ozonide it was warmed on a water bath for two hours. The solution was made faintly alkaline with sodium carbonate after which it was extracted several times with ether. The alkaline solution was then acidified and again extracted with ether. The ethereal solution was dried and the ether removed. The small residue was treated with an aqueous solution of semicarbazide hydrochloride containing enough sodium acetate to neutralize the hydrochloric acid in combination with the semicarbazide. No precipitate was formed. After the reaction mixture was allowed to stand for several days a few crystals separated which after being washed with alcohol melted at 254° C, the melting point of the semicarbazone of pyruvic aldehyde.

Another sample was ozonized according to a method described by Whitmore and Church.¹ A current of ozonized oxygen was passed through an ice cold solution (1.5 g.) of the hydrocarbon in 40 cc. of carbon tetrachloride for eight hours. The zinc-water-catalyst method was used to decompose the ozonide. Ozonizations were conducted at 1-15-0°C. After the ozonide was decomposed the solution was filtered from the zinc and treated with a solution of p-nitro-phenylhydrazine in 2 molar hydrochloric acid solution. The solution was warmed to approximately 60° C. and then allowed to cool. A yellow precipitate which

¹Whitmore and Church, J. Amer. Chem. Soc. 54, 3710 (1932).

turned red on standing was formed in a short while. The residue, insoluble in alcohol, melted at 313° C., the melting point of a mixture of these crystals with synthetic para-nitro-phenylosazone of diacetyl was 315° C. The yield of the phenylosazone amounted to 20 per cent of the theoretical.

In order to determine whether the diacetyl obtained in the ozonization was derived from the supposedly 1,2-dimethyl-cyclobutadiene another sample was ozonized in carbon tetrachloride and the ozonide free from the solvent was treated with 50 cc. of water and the vapor generated (first in the cold and then on gentle warming) was swept by a stream of carbon dioxide into different reagents. No considerable amount of formaldehyde could have been produced since *o*-naphthol and para-nitro-phenylhydrazine gave no derivative. A solution of dimethyldihydroresorcinol, however, gave a small precipitate of crystals which melted at 186° C. indicating that a small amount of formaldehyde was produced.

After proving that the hydrocarbon when oxidized with ozone gives diacetyl as one of the products the experiment was repeated several times in an effort to isolate the other fragment of the molecule, namely, glyoxal or its oxidation product oxalic acid. The method used by Levine and Cole¹ was followed. These investigators have shown that when *o*-xylene is submitted to ozonolysis in various solvents it gives glyoxal, methyl glyoxal, and diacetyl, each of which may be isolated in the form of its *p*-nitrophenylosazone. The method used was briefly this: The hydrolyzed product was treated with a solution of *p*-nitrophenylhydrazine in 2 normal hydrochloric acid solution. The red crystals formed were extracted first with alcohol and then with pyridine. The crystals were completely dissolved by the pyridine (the *p*-nitrophenylosazone of glyoxal is insoluble in pyridine). The crystals were reprecipitated from the pyridine solution with water, washed with alcohol in order to free them from nitrobenzene. They melted at 313° C. and a mixture of this substance with the authentic *p*-nitrophenylosazone of the diacetyl melted at 315° C.

Ozonization of Hydrocarbon in Acetic Anhydride Solution.—

A stream of ozonized oxygen was passed into an ice cold solution of hydrocarbon (1 g.) in 40 cc. of acetic anhydride for twelve

¹Levine and Cole, J. Am. Chem. Soc., 54, 338 (1932).

hours. The ozonide was decomposed by pouring the solution on cracked ice. One-half of this solution was treated with a solution of p-nitrophenylhydrazone in 2 normal hydrochloric acid. A few crystals which melted at 220° C. after being recrystallized from benzene were obtained. The melting point of a mixture of this substance with authentic p-nitrophenylhydrazone of pyruvic acid was not appreciably lowered. Repeated experiments made on different samples of hydrocarbon failed to confirm this experiment.

The other half of the solution was treated with an alcoholic solution of 2,4-dinitrophenylhydrazine.¹ A small precipitate was formed immediately which after being filtered and redissolved in alcohol settled out as needle shaped crystals melting at 147° C., the melting point of the 2,4-dinitrophenylhydrazone of acetaldehyde.

1,4-Dichloro-2,3-dimethyl- Δ^2 butene.—2,3-Dimethylbutadiene (27.4 g.) was dissolved in sodium-dried ether (150 cc.) and a stream of dry chlorine was passed into the solution under strong cooling in a salt ice bath until the theoretical weight of chlorine (for 1 mol) was absorbed. The ether was removed by vaporization. The product was distilled under reduced pressure: a considerable portion distilled over at $28-42^{\circ}$ C. under 10 mm. pressure, while the remainder distilled over at $28-42^{\circ}$ C. under 10 mm. pressure was redistilled. The portion distilling at $72-82^{\circ}$ C. under 10 mm. pressure was redistilled. Most of it distilled at 77° C. under 10 mm. pressure. It solidified when cooled in ice water for a short time. Yield (35 gm.) 68 per cent of the theoretical. This fraction was analyzed for chlorine.

Anal.: Subs., 0.1406, 0.1748; Ag Cl, 0.2659, 0.3278.

Calcd. for $C_6H_{10}Cl_2$: Cl, 46.38. Found: Cl, 46.58, 46.29.

The conditions under which 2,3-dimethylbutadiene was chlorinated were varied. Various solvents such as carbon tetrachloride, chloroform, ligroin, carbon disulphide and glacial acetic acid were used. In one case a solution of chlorine in carbon tetrachloride² was added dropwise to a solution of the

¹Allen, J. Am. Chem. Soc., 52, 2957 (1930).

²Jones and Williams, J. Chem. Soc., 829 (1934).

diene in the same solvent. The temperature was varied from -18° to about 10° C. However, less hydrogen chloride was liberated and larger yields of the dichloride were obtained when the chlorination was carried out at 0° in an ethereal solution of the 2,3-dimethylbutadiene.

The 2,3-dimethylbutadiene dichloride (2 gm.) was dissolved in chloroform and a stream of ozonized oxygen was bubbled through the solution for 25 hours. After ozonization was complete the chloroform was removed by suction and the ozonide decomposed with water. The ozonide was warmed on a water bath for 2 hours to insure complete decomposition. An aqueous solution of semicarbazide hydrochloride containing enough sodium acetate to neutralize the hydrochloric acid in combination with the semicarbazide was added to the cold solution of the decomposed ozonides. A semicarbazone settled out after several hours which melted at 153° C. The yield was 82 per cent of the calculated. A mixture of this substance with synthetic semicarbazone prepared from chloroacetone melted at 153° C. When the solution of the semicarbazone of chloroacetone was heated for a short time a pale yellow halogen free solid melting at 254° C., the melting point of the semicarbazone of pyruvic aldehyde was obtained. No other products could be isolated. This proved that the dichloride is a 1,4-addition compound.

2-3-Dimethylbutadiene dichloride was subjected to ozonization and the ozonide was freed from the solvent in the manner just described. The viscous ozonide was placed in a flask and 50 cc. of water added to it. A stream of carbon dioxide was passed into the solution of the ozonide and then into a solution of β -naphthol in alcohol. No precipitate was formed which indicated that formaldehyde was absent. This is supporting evidence for the absence of the 1,2-dichloride of dimethylbutadiene.

Oxidation with Potassium Permanganate.—A sample of the dichloride in acetone solution was treated with a 5 per cent solution of potassium permanganate. Magnesium sulphate was added to keep the reaction mixture neutral. The solution was filtered from the manganese dioxide and the manganese dioxide was dissolved in a small quantity of sodium bisulphite and sulphuric acid. The combined solutions were freed from acetone by means of a current of air. The solution, freed from acetone, was extracted several times with ether. After the evaporation of the ether a white

solid (3.5 g.) was obtained which melted at 94° C. This corresponds to a 60 per cent yield of the glycol. It was analyzed for chlorine.

Anal.: Subs., 0.1110, 0.1242; Ag Cl, 0.1691, 0.1889.

Calcd. for Cl, 37.94. Found: Cl, 37.65, 37.63.

This indicated that the compound is 1,4-dichloro-2,3-dimethyl, 2-3-dihydroxybutane.

Preparation of 1-Chloro-2,3-Dimethylbutadiene.--When 1,4-dichloro-2,3-dimethylbutene was heated to about 180° C. with twice its weight of powdered potassium hydroxide a vigorous reaction occurred. A small quantity of a low boiling chloride distilled through the condenser which was attached to a receiving flask immersed in a salt ice bath. The product was taken up in ether, the ethereal extract washed and dried over anhydrous calcium sulphate. After several fractionations a colorless liquid was obtained which distilled at 28° C. under 10 mm. pressure. Analysis indicated that it was a mono-chloride of 2,3-dimethylbutadiene.

Anal.: Calcd. for C_6H_8Cl : C, 61.43, H = 7.689,
Cl 30.64.

Found: C, 61.02, H, 7.682, Cl, 30.50, 30.46.

The yield was very small, from 3-5 per cent of the theoretical.

III. SUMMARY

(1) 1,4-dibromo-2,3-dimethyl Δ^2 butene loses 1 molecule of hydrogen bromide from the 1,4 positions to give 1-bromo-2,3-dimethylbutadiene when it is treated with powdered potassium hydroxide or dimethylaniline. Some 2,3-dimethylbutadiene is also formed.

(2) The 1-bromo-2,3-dimethylbutadiene absorbs either one molecule of bromine to give a tribromide or two molecules of bromine to give a pentabromide.

(3) The 1-bromo-2,3-dimethylbutadiene reacts with two molecules of maleic anhydride to give a terpene-like substance which may be hydrolyzed to the corresponding acid.

(4) The 1-bromo-2,3-dimethylbutadiene reacts further with powdered potassium hydroxide to give a very small yield of hydrocarbon which is presumably 1,2-dimethylcyclobutadiene.

(5) The hydrocarbon which we shall call 1,2-dimethylcyclobutadiene reacts with one molecule of bromine to give the corresponding dibromide or with two molecules of bromine to give the tetrabromide derivative.

(6) The 1,2-dimethylcyclobutadiene reacts with hypobromous acid to give a bromhydrin.

(7) An attempt was made to determine the structure of the hydrocarbon (1,2-dimethylcyclobutadiene) by ozonization but the results were anomalous. Diacetyl was isolated but no glyoxal or oxalic acid could be detected in the fragments of ozonization. In one experiment rather conclusive evidence for pyruvic acid as one of the oxidation products was obtained. Subsequent ozonization experiments failed to indicate that pyruvic acid is one of the products yielded when the hydrocarbon is oxidized with ozone or potassium permanganate.

(8) 2,3-Dimethylbutadiene reacts with hypobromous acid to form a stable bromhydrin whose structure was proved to be a 1,4-derivative by ozonization.

(9) By chlorination of 2,3-dimethylbutadiene a dichloride was formed which was proved by ozonization to be 1,4-dichloro-2,3-dimethyl- Δ^2 -butene.

(10) The 1,4-dichloro-2,3-dimethyl- Δ^2 -butene loses a molecule of hydrogen chloride to form a very small quantity of a mono-chloride of 2,3-dimethylbutadiene when it is heated with powdered potassium hydroxide.

(11) The 1,4-dichloro-2,3-dimethyl- Δ^2 -butene was oxidized to the corresponding dihydroxy compound by an acetone solution of potassium permanganate.

